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CLAIMS

[Claim(s)]

[Claim 1] The water-soluble antireflection film ingredient characterized by including the alkylamine or alkanolamine by which the fluorine permutation of a part or all of a hydrogen atom of a hydrocarbon group was carried out. [Claim 2] The water-soluble antireflection film ingredient characterized by using as a principal component the perfluoro compound which contains the alkylamine according to claim 1 or the alkanolamine by which the fluorine permutation was carried out as a counter cation.

[Claim 3] The water-soluble antireflection film ingredient according to claim 2 with which a perfluoro compound is

chosen from what is shown by following general formula (1) - (16).

[Formula 1]
$$CF_3$$
— $COOM$ (1)

$$MOOC$$
— (CF_2) — $COOM$ (2)

$$CF_{3} \xrightarrow{\left(OCF - CF_{2}\right)_{c}} \left(OCF_{2}\right)_{d} \left(OCF_{2}CF_{2}\right)_{e} COOM$$
 (3)

$$MOOO - F_2O - OCF_2 - CF_2 - \frac{1}{f} - OCF_2 - \frac{1}{g} - COOM$$
 (4)

$$F \xrightarrow{CF_2CF_2O} \xrightarrow{h} \left(CF_2CF_2O \xrightarrow{j} CF_2CF_2O \xrightarrow{j} CF_3 \right)$$

$$MOOC-CF \xrightarrow{CF_2CF_2CF_2CF_2C} CF_2CF_2C) \xrightarrow{I} (CF_2CF_2C) \xrightarrow{I} (CF_2CF_2C) \xrightarrow{I} CF_3CF_3$$
(6)

$$\frac{\left(\text{CF}_{2}\text{CF}_{2}^{-}\right)_{o}\left(\text{CF}_{2}\text{CF}\right)_{p}}{\left(\text{CF}_{2}\text{CF}_{2}^{-}\right)_{q}\left(\text{CF}_{2}\text{CF}_{2}^{-}\right)_{r}\left(\text{CF}_{2}^{-}\right)_{s}}\text{COOM} \qquad (7)$$

$$\begin{array}{c}
-\left(-CF_{2}CF_{2}\right) + \left(-CCF_{2}\right) & (8) \\
CF_{2} & (6) \\
CF_{2} & (6)
\end{array}$$

[Formula 2]

$$CF_3 - (CF_2)_{\overline{a}} - SO_3M \tag{9}$$

$$\dot{MO}_3S - (\dot{C}F_2)_b SO_3M$$
 (10)

$$CF_{3} \xrightarrow{OCF-CF_{2}}_{C} \xrightarrow{OCF_{2}}_{d} \xrightarrow{OCF_{2}CF_{2}}_{e} SO_{3}M$$

$$(11)$$

$$MO_3S - F_2C - OCF_2 - CF_2 - \int_f \left(-OCF_2 - \int_g SO_3M \right)$$
 (12)

$$F \leftarrow CF_2O \rightarrow CF_2O \rightarrow CF_2O \rightarrow CF_3CF_3O_3M$$
 (13)

$$MO_{3}S - CF - \left(OCF_{2}CF_{2}\right) - \left(CF_{2}CF_{2}O\right) - \left(CF_{2}O\right) - \left$$

$$\frac{\left(\text{CF}_{2}\text{CF}_{2}\right)_{o} \cdot \left(\text{CF}_{2}\text{CF}\right)_{p}}{\left(\text{OCF}_{2}\text{CF}_{2}\right)_{q} \left(\text{OCF}_{2}\text{CF}_{2}\right)_{r} \left(\text{CF}_{2}\right)_{s} \text{SO}_{3}\text{M}} \qquad (15)$$

$$\text{CF}_{3}$$

$$\begin{array}{c}
-\left(-CF_{2}CF_{2}\right) t - \left(-O - C \right) u \\
CF_{2} \\
SO_{3}M
\end{array}$$
(16)

the inside of a formula, and a and b -- the integer of 0-20, and c, d, e, f, g, h, i, j, k, l, m and n -- the integer of 0-15 -- as for 0-100, and p and u, o and t show the alkylamine or alkanolamine by which, as for 1-100, and q, r and s, the integer of 0-15 was carried out, and, as for M, the fluorine permutation of a part or all of a monovalent hydrocarbon radical of a hydrogen atom was carried out. [of carbon numbers 1-20]

[Claim 4] The pattern formation approach characterized by removing the above-mentioned light reflex prevention layer after forming the light reflex prevention layer which consists of a light reflex prevention film ingredient according to claim 1, 2, or 3 as the upper layer of a photoresist layer and exposing the above-mentioned resist layer through this light reflex prevention layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the approach of forming a resist pattern using the light reflex prevention film ingredient and this which make highly precise micro processing possible also on an irregular base in the photolithography which used the photoresist.

[0002]

[Description of the Prior Art] While detailed-ization of a pattern rule is called for with high integration and high-speedizing of LSI in recent years, in the optical exposure used as a current general-purpose technique, the limitation of the

essential resolution originating in the wavelength of the light source is approached.

[0003] As an exposure light used in the case of resist pattern formation, the optical exposure which makes the light source g line (436nm) or i line (365nm) of a mercury-vapor lamp is used widely, and has been confirmed as a means for the further detailed-izing by the approach of short-wavelength-izing exposure light. For this reason, instead of i line (365nm), the KrF excimer laser (248nm) of short wavelength came to be used for the mass-production process of 64 M bit (processing dimension is 0.25 micrometers or less) DRAM (dynamic random access memory) as the exposure light source. However, the light source of short wavelength is needed more for manufacture of degree-of-integration 256M and DRAM beyond 1G which need a still more detailed processing technique (a processing dimension is 0.2 micrometers or less), and the photolithography especially using an ArF excimer laser (193nm) has been examined. [0004] In the phase in early stages of KrF lithography, the stepper of the combination of an achromatic lens or a reflecting optical system, and broadband light was developed. However, since the precision of the catoptric system of an achromatic lens or the aspheric surface was not enough, the homogeneous light and the combination of a dioptricsystem lens became in use. half here -- in - wavelength exposure, the light which carries out incidence, and the reflected light from a base interfering, and generating a standing wave is the phenomenon known well for many years. The standing wave caused dimension fluctuation of the line breadth of a pattern etc., collapse of a configuration, etc. [0005] On the other hand, use of the coherent homogeneous light made a standing wave and halation amplify further with short wavelength-ization.

[0006] Conventionally, the approach of putting an extinction agent into a resist ingredient, and the method (BARC law, JP,62-159143,A) of covering a resist layer top face (ARCOR law, JP,62-62520,A, JP,62-62521,A, JP,60-38821,A) and a base side with an antireflection film were proposed as an approach of stopping a standing wave. The ARCOR method is the approach of forming a transparent antireflection film in the resist layer upper part, and being an approach including the process which exfoliates after exposure, and forming a detailed pattern with high high degree of accuracy and doubling precision by the simple approach. If the perfluoroalkyl compound (a perfluoroalkyl polyether, perfluoro alkylamine) of a low refractive-index ingredient is used as an antireflection film, the reflected light of a resist-

antireflection film interface will decrease sharply, and dimensional accuracy will improve.

[0007] However, although chlorofluocarbon etc. is used for the diluent for the above-mentioned perfluoroalkyl compound to control spreading thickness since compatibility with the organic substance is low, as for chlorofluocarbon, the use poses a problem from a viewpoint of current environmental preservation as everyone knows. Moreover, the above-mentioned compound has a problem in uniform membrane formation nature, and was not able to say that it was enough as an antireflection film. Moreover, the antireflection film had to be exfoliated by chlorofluocarbon before the development of a photoresist layer. Therefore, the demerit that must extend the system for antireflection film exfoliation to equipment conventionally, and the cost of a chlorofluocarbon system solvent increases considerably etc. and in respect of practical use was large.

[0008] When it is going to exfoliate an antireflection film without extension to equipment conventionally, exfoliating using a development unit is most desirable. It can be said that its antireflection film ingredient which can exfoliate easily with these solutions is desirable since the solution used in the development unit of a photoresist is pure water which is the alkali water solution which is a developer, and a rinse. Therefore, the pattern formation approach using much water-soluble antireflection film ingredient and these was proposed. For example, JP,6-273926,A, 6-289620, 7-160002, 7-181684, 7-234514, 7-295210, 7-333855, 8-44066, 8-95253, 8-179509, 8-292562, 8-320569, 9-50129, 9-90615, 9-236915, 9-258452, 9-258453, 9-291228, 9-325500, 10-3001, 10-17623, 10-69091, 11 No. -124531 official report, Patent 2643056th and a No. 2878150 or 2803549 official report are illustrated.

[0009] Here, the refractive index of the upper antireflection film for setting a standing wave to 0 has the ideal square root of the refractive index of a resist layer. Since the refractive index of the resist layer of a polyhydroxy styrene system used by KrF is 1.8, ideal value is 1.34. Since a ring is lost, generally compared with an aromatic series system polymer, as for the alicycle group system resist layer used for ArF, a refractive index falls. For example, in polyacrylate, it is set to 1.6 and ideal value falls even to 1.27. Although the ingredient with such a low refractive index is limited to the ingredient of a Teflon system, it is needed that the upper antireflection film is a water-soluble ingredient as above-mentioned at the time of alkali development since the direction which can exfoliate is advantageous in process. However, in order to make a hydrophobic high perfluoro system ingredient into water solubility very much, when the hydrophilic substituent was introduced, the refractive index increased and the value before and behind 1.5 was [in / at the conventional thing / in KrF / 1.42 order and ArF] a limitation. The effect of a standing wave is suppressed only in the combination of an extinction agent and the upper antireflection film, and it is becoming impossible therefore, to control a dimension by patterning 0.20 micrometers or less with KrF lithography. In ArF lithography, it is thought that decline in the further refractive index is needed for said reason if the effectiveness of the upper antireflection film can hardly be expected but management of line breadth will become severe by contraction of the further line breadth also in KrF in the present condition from now on.

[0010] The antireflection film prepared in a lower layer can acquire the high acid-resisting effectiveness to the antireflection film of the resist upper layer. The bottom of it can reduce the reflection from a base to 1% or less by setting the ingredient of the optimal refractive index (n value) and an absorbancy index (k value) as suitable thickness in the case of high reflective bases [, such as p-Si and aluminum,], and the antireflection film of a substrate can demonstrate very big effectiveness. For example, as 1.8, if the refractive index of a resist layer sets it as the exposure wavelength of 248nm, n1.5, k0.55, and 55nm of thickness, it can do a reflection factor to 0.5% or less. However, when a level difference is in a substrate, the thickness of an antireflection film is sharply changed on a level difference. Although the acid-resisting effectiveness of the first base whose cross protection is strong 50-60nm is also so high since not only the absorption of light but cross protection is used for the acid-resisting effectiveness of a substrate, a reflection factor is sharply changed by fluctuation of thickness, the ingredient which raised the conformal nature which raised the molecular weight of the base polymer use for an antireflection film ingredient, and suppressed the thickness fluctuation on a level difference is also propose -- **** (JP,10-69072,A) -- if the molecular weight of a base polymer becomes high, since it said that it is limit to a level difference with comparatively low height, the problem the pinhole behind a spin coat becomes easy to generate, and the problem of it become impossible to filter arise, and omnipotent cannot demonstrate conformal nature.

[0011] Then, the thickness of an antireflection film is raised and, generally the approach fluctuation of the reflection factor by thickness fluctuation adopts comparatively small thickness (80nm or more) is taken. Moreover, the substrates of an antireflection film are transparent membranes, such as silicon oxide and a nitride, and though flattening of the front face of a transparent membrane was carried out by CMP etc. when a level difference was under the transparent membrane further, the part to which reflection becomes high appears. In order to stabilize a reflection factor also in this case, it is necessary to use thickness of an antireflection film as a thick film 80nm or more like the above-mentioned. However, if the antireflection film of a substrate is set as 80nm or more, a reflection factor will rise and the reflection which is a maximum of 4% will occur. In dimension control of micro-machining 0.20 micrometers or less, the reflection factor had to be made at least 2% or less, and the limitation is generated only with the antireflection film of a substrate. However, it is thought that it can decrease further by concomitant use with the upper antireflection film, and the further decline in the refractive index of the upper antireflection film is demanded.

[0012] Furthermore, the upper antireflection film has not only the function as an original antireflection film but the function as atmospheric isolation film after exposure or the function to prevent a development defect by raising compatibility with a developer, and is considered to become an ingredient more important future still. [0013] As an antireflection film for ArF, there is a problem of not only the problem of the above-mentioned refractive index but permeability. As a result of this invention persons' examining many things, it turned out that strong absorption has most antireflection films developed for KrF to ArF light.

[0014] If there is absorption strong against the upper antireflection film, since light will not reach a lower layer resist, the problem that sensibility falls arises. Although it is known that aromatic series, such as a phenyl group, and unsaturated hydrocarbon radicals, such as a vinyl group, have strong absorption to ArF light, carboxylic amide etc. has strong absorption. For this reason, the amine salt of a carboxylic acid, the thing which added the fluorochemical surfactant or fluorine system polymer containing carboxylic amide, and has lowered the refractive index, or the thing which is using the polyvinyl pyrrolidone as a binder polymer carried out the knowledge of the ability not to use to ArF as a hydrophilic substituent.

[0015] Moreover, although using ethyleneoxide, propylene oxide, alcohol, an amine, etc. as a hydrophilic radical is also considered, it neutralized with the acid generated from the resist, and the amine became T-top profile, and other

things were mixed with the resist and have caused mixing.

[0016] This invention was made in view of the above-mentioned situation, it is detailed, and dimensional accuracy and its doubling precision are high, and is simple, and does not have an environmental problem, either, and productivity is high and it aims at offering the formation approach of the light reflex prevention film ingredient for forming a resist pattern with sufficient repeatability, and the resist pattern using this.

[The means for solving a technical problem and the gestalt of implementation of invention] In order that this invention persons may attain the above-mentioned purpose, as a result of inquiring wholeheartedly, fluorination alkylamine or alkanolamine, By using the light reflex prevention film containing the perfluoro compound which contains especially fluorination alkylamine or alkanolamine as a counter cation The reflected light in a resist layer front face was reduced without loss of incident light, and the fall of the pattern dimensional accuracy by optical multiple echo interference in a resist layer could be prevented, and, moreover, the knowledge of the ability to also perform exfoliation simple with water or an alkali developer was carried out. That is, according to examination of this invention persons, that it is effective adding a perfluoro amine as a counter cation of a hydrophilic substituent turned out to be decline in the further refractive index for the improvement in transparency in an ArF excimer laser. Although carboxylic amide and the amine salt of a carboxylic acid had absorption strong against 193nm as above-mentioned, the perfluoro amine salt of a carboxylic acid has small absorption, and the knowledge of a refractive index falling, when a fluorine content increases is carried out, and it came to make this invention.

[0018] therefore, with this invention suitable as base resin of the antireflection-film ingredient used for micro processing in production processes, such as a semiconductor device The water-soluble antireflection film ingredient containing the water-soluble polyperfluoro alkyl ingredient which has a sulfonyl group in a side chain, And it is a thing about the pattern formation approach suitable in case high energy lines, such as far ultraviolet rays, KrF excimer laser light (248nm), and ArF excimer laser light (193nm), are used as the exposure light source. (1) The water-soluble antireflection film ingredient characterized by including the alkylamine or alkanolamine by which the fluorine permutation of a part or all of a hydrogen atom of a hydrocarbon group was carried out, (2) The water-soluble antireflection film ingredient characterized by using as a principal component the perfluoro compound which contains the alkylamine or alkanolamine by which the fluorine permutation was carried out [above-mentioned] as a counter cation, (3) The light reflex prevention layer which consists of the above-mentioned light reflex prevention film ingredient as the upper layer of a photoresist layer is formed, and after exposing the above-mentioned resist layer through this light reflex prevention layer, the pattern formation approach characterized by removing the abovementioned light reflex prevention layer is offered.

[0019] Hereafter, lessons is taken from this invention and it explains in more detail. As for the water-soluble antireflection film ingredient of this invention, it is desirable to use as a principal component the perfluoro compound with which a part or all of a hydrogen atom of a hydrocarbon group contains especially this alkylamine or alkanolamine by which the fluorine permutation was carried out as a counter cation including the alkylamine or alkanolamine by

which the fluorine permutation was carried out.

[0020] As the above-mentioned alkylamine and alkanolamine, carbon numbers 1-20 and a thing with especially 1-10 may be desirable as a monovalent hydrocarbon radical, especially an alkyl group, and amines may be any of the 1st class, the 2nd class, and the 3rd class. As an example of the alkylamine by which the fluorine permutation was carried out, and alkanolamine, perfluoro triethylamine, perfluoro triethylamine, perfluoro tributylamine, perfluoro pentylamine, trifluoro ethylamine, trifluoro propylamine, 4 and 4, and 4-trifluoro-DL-valine, 5 and 5-trifluoro-DL-leucine etc. is mentioned.

[0021] As the above-mentioned perfluoro compound, what is shown by following general formula (1) - (16) is

mentioned.

[0022]

[Formula 3]
$$CF_3$$
— $COOM$ (1)

$$MOOC-(CF_2) - COOM$$
 (2)

$$CF_3 + CF_2 + CF_2 + COOM$$

$$CF_3 + CF_2 + COOM$$

$$CF_3 + COOM$$

$$CF_4 + COOM$$

$$CF_5 + COOM$$

$$MOOC - F_2C \left(OCF_2 - CF_2\right)_f \left(OCF_2\right)_g COOM$$
 (4)

$$F \xrightarrow{CF} CF_2O \xrightarrow{h} \left(CF_2O \xrightarrow{j} \left(CF_2CF_2O \xrightarrow{j} CF COOM \right) \right)$$
 (5)

$$\begin{array}{c} \text{MOOC-CF-}(OCF_2CF_{2}) \\ CF_{3} \\ CF_{3} \end{array} \\ \begin{array}{c} CF_{2}CF_{2}O \\ CF_{3} \\ CF_{3} \end{array} \\ \begin{array}{c} CF_{2}CF_{2}O \\ CF_{3} \\ CF_{3} \\ CF_{3} \\ CF_{3} \end{array} \\ \begin{array}{c} CF_{3}CF_{3} \\ CF_{3} \\ CF_{4} \\ CF_{5} \\$$

$$\frac{-\left(\text{CF}_{2}\text{CF}_{2}^{-}\right)_{o} - \left(\text{CF}_{2}\text{CF}\right)_{p}}{\left(\text{OCF}_{2}\text{CF}_{2}^{-}\right)_{r} \left(\text{CF}_{2}^{-}\right)_{s} \text{COOM}} \tag{7}$$

[0023] [Formula 4]

$$CF_3 - (CF_2)_{\overline{a}} SO_3M \tag{9}$$

$$MO_3S - (CF_2)_b - SO_3M$$
 (10)

$$CF_{3} \xrightarrow{OCF-CF_{2}}_{C} \xrightarrow{OCF_{2}}_{d} \xrightarrow{OCF_{2}CF_{2}}_{e} SO_{3}M$$
(11)

$$MO_3S - F_2C - OCF_2 - CF_2 - \int_f \left(-OCF_2 - \int_g SO_3M \right)$$
 (12)

$$F \xrightarrow{CF} CF_2O \xrightarrow{h} \left(CF_2O \xrightarrow{j} \left(CF_2CF_2O \xrightarrow{j} CF - SO_3M \right) \right)$$

$$CF_3$$

$$CF_3$$

$$CF_3$$

$$CF_3$$

$$MO_{3}S - CF - CF_{2}CF_{2}CF_{3} - CF_{2}CF_{2}O + CF_{2}CF_{2}O + CF_{2}CF_{2}O + CF_{3}CF_{3}M$$

$$CF_{3} - CF_{3} - CF_{3}CF_{3}$$

$$(14)$$

$$\frac{\left(\text{CF}_{2}\text{CF}_{2}\right)_{o}}{\left(\text{CF}_{2}\text{CF}\right)_{q}}\left(\text{CF}_{2}\text{CF}_{2}\right)_{r}\left(\text{CF}_{2}\right)_{s}\text{SO}_{3}M} \qquad (15)$$

$$\frac{\left(\text{CF}_{2}\text{CF}_{2}\right)_{o} \left(\text{CF}_{2}\text{CF}\right)_{p}}{\left(\text{OCF}_{2}\text{CF}\right)_{q}\left(\text{OCF}_{2}\text{CF}_{2}\right)_{r}\left(\text{CF}_{2}\right)_{s}\text{SO}_{3}M} \qquad (15)$$

$$\frac{\text{CF}_{3}}{\text{CF}_{2}} \left(\text{CF}_{2}\right)_{t} \left(\text{CF}_{2}\right)_{t} \left(\text{CF}_{2}\right)_{s}\text{SO}_{3}M} \qquad (16)$$

the inside of a formula, and a and b -- the integer of 0-20, and c, d, e, f, g, h, i, j, k, l, m and n -- the integer of 0-15 -- as for 0-100, and p and u, o and t show the alkylamine or alkanolamine by which, as for 1-100, and q, r and s, the integer of 0-15 was carried out, and, as for M, the fluorine permutation of a part or all of a monovalent hydrocarbon radical of a hydrogen atom was carried out. [of carbon numbers 1-20]

[0024] Here, M shows the alkylamine or alkanolamine by which the fluorine permutation of a part or all of a hydrogen atom of the monovalent hydrocarbon radical of carbon numbers 1-20, especially an alkyl group was carried out, and the above-mentioned thing is illustrated.

[0025] Moreover, in a formula (1), (2), (9), and (10), in the integer of 0-20, especially 3-15, a formula (3), and (11), c, d, and e of a and b are the integers of 0-15, especially 0-10, and, as for c+d+e, it is desirable 1-10, and that it is especially 1-8. In a formula (4) and (12), f and g are the integers of 0-15, especially 0-10, and, as for f+g, it is desirable 1-10, and that it is especially 1-8. In a formula (5) and (13), h, i, and j are the integers of 0-15, especially 0-10, and, as for h+i+j, it is desirable 1-10, and that it is especially 1-8. In a formula (6) and (14), k, l (El), m, and n are the integers of 0-15, especially 0-10, and, as for k+1+m+n, it is desirable 1-10, and that it is especially 1-8.

[0026] In the polymer of a formula (7), (15) and (8), and (16), when referred to as p= 1, o is the integer of 0-50, especially 0-30, q, r, and s are the integers of 0-15, especially 0-10, and, as for q+r+s, it is desirable 1-20, and that it is especially 1-10. the case where u is set to 1 -- t -- 0-100 -- desirable -- 0-50 -- it is 0-30 still more preferably. [0027] In addition, as for the alkylamine by which M was fluorinated, and alkanolamine, it is desirable for 0.01-10 mols to add to the carboxyl group or one mol of sulfonic groups of a perfluoro compound shown by general formula (1

[0028] The antireflection-film ingredient of this invention of carrying out 0-300 weight section addition of various kinds of water-soluble polymers, for example, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, a polyvinyl pyrrolidone, polyethylene oxide, an amylose, a dextran, a cellulose, the pullulan, etc. to the above-mentioned perfluoro compound 100 weight section is arbitrary in order to raise membrane formation nature.

[0029] Into the antireflection film ingredient of this invention, the surfactant commonly used in order to raise spreading nature can be added. In addition, the addition can usually be made into an amount in the range which does not bar the effectiveness of this invention.

[0030] Here, as a surface active agent, perfluoroalkyl polyoxyethylene ethanol, fluorination alkyl ester, a perfluoro alkylamine oxide, a fluorine-containing ORGANO siloxane system compound, etc. are mentioned. For example, Fluorad "FC-430", "FC-431" (all are the Sumitomo 3M make), Sir chlorofluocarbon "S-141", "S-145", "S-381", "S-383" (all are the Asahi Glass Co., Ltd. make), A uni-dyne "DS-401", "DS-403", "DS-451" (all are the Daikin Industries, LTD. make), A megger fuck "F-8151", "F-171", "F-172", "F-173", "F-177" (all are the products made from Dainippon Ink Industry), "X-70-092", "X-70-093" (all are the Shin-Etsu Chemical Co., Ltd. make), etc. can be mentioned. Preferably, Fluorad "FC-430" (Sumitomo 3M make) and "X-70-093" (Shin-Etsu Chemical Co., Ltd. make) are mentioned.

[0031] Moreover, a water-soluble antireflection-film ingredient tends to generate a bubble, and the detailed bubble of the micron unit called a microbubble is said to generate a pattern defect. In order to reduce a microbubble, the approach of adding a defoaming agent is common. As a defoaming agent for water solutions, although long-chain alcohols, such as natural oil fat, such as soybean oil, corn oil, olive oil, linseed oil, castor oil, and lard oil, amyl alcohol, and octyl alcohol, and silicone resin are generally known, these things are ingredients which hydration is low or are not hydrated at all. Although said ingredient is excellent in antifoam, when adding into a water-soluble ingredient and forming membranes by spin coating, coating nonuniformity arises and it cannot be formed to homogeneity. In order to form membranes to homogeneity by spin coating, a defoaming agent with high hydration is required, the acetylene series defoaming agent shown as a high defoaming agent of hydration in this invention by alcohols, such as a methanol, ethanol, isopropyl alcohol, n-butyl alcohol, n-hexyl alcohol, and ethylene glycol, or the following general formula (17), and (18) -- **** for effective doses -- things are made.

$$\begin{array}{c|c}
R^7 \\
R^8 - C - C = C - R^9 \\
\hline
0 \\
R^{10} \\
0 \\
Z
\end{array}$$
(18)

[0033] Here, the alkylene group of carbon numbers 1-10, x, and y and z of a hydrogen atom that R1, R2, R3, R4, R7, and R8 are the same respectively or of a different kind or the alkyl group of carbon numbers 1-20, and R5, R6 and R10 are the integers of 0-20.

[0034] In order to form a resist pattern using the light reflex prevention film ingredient of this invention, the lithography process which can adopt a well-known approach, for example, is shown in drawing 1 can perform. First, depending on (A) and the case, it prebakes by forming a photoresist layer 2 by the approach of a spin coat etc. on the base 1 upper layer, and the light reflex prevention film ingredient of this invention is applied by the approach of a spin coat etc. on this photoresist layer 2, it prebakes further depending on the case, and the light reflex prevention layer 3 is formed (B). The ultraviolet rays 4 with a wavelength of 180-500nm can be exposed by the reduced-projection-exposure method in the light reflex prevention layer 3 at a pattern configuration, namely, A part can be exposed in drawing 1 (C), subsequently the light reflex prevention layer 3 can be removed, and a resist pattern 5 can be formed by the approach of developing using a developer (D). After exposure, although postexposition JUABEKU (PEB) may be performed depending on the case, when a resist layer is a chemistry magnification mold resist layer, a PEB process becomes indispensable. In this case, PEB may be performed after removing a light reflex prevention layer, and a light reflex prevention layer may be removed after PEB.

[0035] In addition, pure water can be used as a diluent of a light reflex prevention film ingredient. Furthermore, use of the usual photoresist development unit is possible for removal of a light reflex prevention layer, and it can carry out a rinse with pure water, and if it is exfoliation after PEB, it can exfoliate in development and coincidence.

[0036] If the optical reduction effectiveness of the light reflex prevention film of this invention is explained with reference to drawing 2 and 3, as shown in drawing 2, only by forming the resist layer 2 in a base 1 here While the reflection Ir1 with incident light I0 remarkable at an air-resist interface takes place and the amount of incident light loses Since it is repeated that the light which entered in the resist layer 2 takes reflective Ir2 by the resist layer-base interface, and this reflected light Ir2 takes reflective Ir3 again by the resist layer-air interface, an optical multiple echo interference arises in a resist layer.

[0037] As shown in drawing 3, on the other hand, by forming the light reflex prevention film 3 of this invention on the resist layer 2 Since the reflection Ir4 by the air-light reflex prevention film interface of incident light I0 and the reflection Ir5 by the light reflex prevention film-resist layer interface can be reduced, loss of the amount of incident light decreases. Moreover, since the thickness of the light reflex prevention membrane layer 3 is set up so that the phase of light may become reverse, Ir6 and Ir7 are weakened mutually, and an optical multiplex interference within the resist layer 2 is controlled.

[0038] From the principle of acid resisting, a reflection factor decreases and the effect of a standing wave can be reduced, so that it will bring refractive-index n' of the light reflex prevention film close to rootn and the thickness will be close brought by odd times lambda/4n', if wavelength of n and exposure light is set to lambda for the refractive index to the exposure light of a resist.

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely

hereafter, this invention is not restricted to the following example.

[0040] Polyvinyl alcohol of 1g [of fluorine compounds of F1-F6, and F9-F14 shown in the [example of example and comparison] following], molecular-weight 80 and 000, and 60% of saponification degrees 0.7g was enough dissolved in 40g of pure water, it filtered with the filter of 0.1-micrometer size, and the antireflection film solution was created. Moreover, 1g of fluorine high molecular compounds of following F7, and F8, F15, F16 and F17 was enough dissolved in 40g of pure water, it filtered with the filter of 0.1-micrometer size, and the antireflection film solution was created. As an example of a comparison, polyvinyl alcohol of 1g [of fluorine compounds of F18-F23 shown below], molecular-weight 80 and 000, and 60% of saponification degrees 0.7g was enough dissolved in 40g of pure water, it filtered with the filter of 0.1-micrometer size, and the antireflection film solution was created. Furthermore, following F24 and 1g of fluorine high molecular compounds shown by F25 were enough dissolved in 40g of pure water, it filtered with the filter of 0.1-micrometer size, and the antireflection film solution was created. [0041] next, dispensing of the sample 1 is carried out on a 8 inch wafer, and a silicon wafer or a synthetic quartz wafer

is first rotated for 20 seconds by 4,000rpm after that for 3 seconds by 300rpm -- making -- the antireflection film of 46nm of thickness -- forming -- a spectrum -- permeability was measured with thickness, the refractive index, and the spectrophotometer by ellipsometry. A result is shown in Tables 1 and 2. From this result, the antireflection film ingredient of this invention has checked high permeability and a low refractive index also not only in KrF but in ArF.

[0042]

[Formula 6]

[Formula 7]

[0044] [Formula 8]

CF ₃ —(CF ₂)—COO ⁻ N(CH ₂ CH ₃) ₃ ⁺	F-18
†(CH3CH2)3N-OOC(CF2)-8COO-N(CH2CH3)3+	F-19
CF ₃ (OCF-CF ₂) ₃ COO ⁻ N(CH ₂ CH ₃) ₃ ⁺	F-20
/ \ /	N/OU-CU-b+
*(CH ₃ CH ₂ N)*OOC-F ₂ C-(OCF ₂ -CF ₂ -)2 (OCF ₂ -)3 OCF ₂ -COOT	N(OFZOFB/3
, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	F-21
F-(CF-CF ₂ O-) ₃ COO ⁻ N(CH ₂ CH ₃) ₃ ⁺	F-22
+(CH ₃ CH ₂)N-OOC-CF-(OCF ₂ CF-) ₂ (O-CF ₂ CF ₂) ₂ (CFCF ₂ O-) ₂ CF- CF ₃ CF ₃ CF-	-COO_N(CH5CH3)3_
0F ₂ \	3
OF3 OF3	F-23
$\frac{-(CF_{2}CF_{2}-)_{5}-(CF_{2}CF-)_{1}}{(CF_{2}CF_{2})_{1}-(CF_{2}CF_{2}-)_{2}}COO^{T}N(CH_{2}CH_{3})_{3}^{+}$	F-24 Mw100,000
CF ₂ CF ₂ -) ₁ (O-C-) ₁ CF ₂ COO-N(CH ₂ CH ₃) ₃ +	F-25 Mw800,000
[0045] [Table 1]	

反射防止用	豆 射防 北田 屈折率		透過率	
・フツ無材料	248nm	193nm	248nm	193nm
F-1	1. 40	1. 58	98%	90%
F-2	1. 41	1. 58	98%	88%
F-3	1. 38	1. 50	98%	90%
F-4	1. 41	1. 58	98%	87%
F-5	1. 39	1, 50	98%	90%
F-6	1. 39	1. 50	98%	89%
F-7	1. 37	1. 49	98%	96%
. F−8	1. 38	1. 50	98%	95%
F-9	1. 40	1. 57	98%	96%
F-10	1. 42	1. 59	98%	95%
F-11	1. 38	1. 50	98%	94%
F-12	1. 40	1. 56	97%	97%
F-13	1. 38	1. 51	97%	98%
F-14	1. 39	1. 50	98%	96%
F 15	1. 33	1. 42	98%	96%
F-16	1. 32	1. 41	98%	95%
F-17	1. 32	1. 42	98%	95%

[0046] [Table 2]

1 4016 2				
反射防止用	屈折率		透過率	
フッ素材料	248nm	193nm	248nm	193nm
F-18	1. 43	1. 60	98%	75%
F-19	1. 44	1. 62	98%	70%
F-20	1. 43	1, 55	98%	73%
F-21	1. 46	1. 65	98%	66%
F-22	1. 43	1. 58	98%	70%
F-23	1. 44	1. 53	98%	68%
F-24	1. 42	1. 52	98%	76%
F-25	1. 41	1. 53	98%	72%
				

[0047] Subsequently, the spin coat of the photoresist SEPR401 (Shin-Etsu Chemical Co., Ltd. make, 30%/micrometer of film transmission) for KrF lithography was carried out changing an engine speed on 8 inches Si base, and it was prebaked on the temperature of 100 degrees C, and the conditions for time amount 90 seconds. Dispensing of the antireflection-film solution which used F16 on it was carried out, the wafer was first rotated for 20 seconds by 4,000rpm after that for 3 seconds by 300rpm, and the antireflection film was formed.

[0048] KrF EKIE -- sima -- the pattern with which Rhine and tooth-space width of face are set to 0.20 micrometers by the laser stepper, respectively was exposed, postexposition JUABEKU was carried out in temperature [of 110 degrees C], and time amount 90 seconds after that, the developer of 2.38 % of the weight of tetramethylammonium hydroxide performed temperature of 23 degrees C, quiescence paddle development was performed in time amount 60 seconds, and the pure-water rinse was performed. A result is shown in drawing 4. From the result of drawing 4, it has checked that it was possible to stop the amplitude of the line breadth by the standing wave by using the antireflection film ingredient of this invention.

[0049]

[Effect of the Invention] The light reflex prevention film ingredient of this invention is detailed, and dimensional accuracy and its doubling precision are high, and it can form a resist pattern with sufficient repeatability.

[Translation done.]

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